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Kinetic Study on S_NAr Reactions of 1-Substituted-4-phenoxy-2,4-dinitrobenzenes with Azide Ion: Effect of Changing Nucleophile from Hydroxide to Azide Ion on Reaction Mechanism and Reactivity

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Abstract

Second-order rate constants ($k_{\text{N}_3\text{Ar}}$) for $\text{S}_{\text{N}}\text{Ar}$ reactions of 1-(Y -substitutedphenoxy)-2,4-dinitrobenzenes (**2a–2h**) with in 80 mol % H_2O /20 mol % DMSO at $25.0 \pm 0.1^\circ\text{C}$ have been measured spectrophotometrically. The Brønsted-type plot is linear with $\rho = 0.38$. The Hammett plots correlated with σ and σ^+ constants exhibit highly scattered points. In contrast, the Yukawa–Tsuno plot results in an excellent linear correlation with $\rho = 1.02$ and $r = 0.51$, indicating that a negative charge develops partially on the O atom of the leaving Y -substitutedphenoxy moiety in the transition state. Accordingly, the reactions have been concluded to proceed through a stepwise mechanism, in which expulsion of the leaving group occurs in the rate-determining step. Comparison of $k_{\text{N}_3\text{Ar}}$ with the k_{OHAr} values reported previously for the corresponding reactions with OH^- has revealed that **2a–2h** are only 6- to 26-fold less reactive than OH^- toward substrates **2a–2h**, although the former is over 11 pK_{a} units less basic than the latter. Solvation and polarizability effects have been suggested to be responsible for the unusual reactivity shown by OH^- . Effects of changing nucleophile from OH^- to N_3^- on reaction mechanism and reactivity are discussed in detail.

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static.pingdom.net/prum.min.js';s.parentNode.insertBefore(p,s);})();
```